

MICROSTRUCTURE TRANSFORMATION DURING MICROEMULSION AND MICELLAR POLYMERIZATIONS

Emulsion polymerization is the most widely used process to prepare polymer colloids (latexes) of sizes 100 to 10,000 nm, finding use in applications such as paints and adhesives. Microemulsion systems contain larger amounts of surfactant relative to the monomer and produce much smaller polymer particles of 20 to 50 nm diameter. The surfactant molecules themselves can be functionalized and polymerized producing even smaller structures of 3 to 5 nm, still retaining a well-defined shape. The reduced size and increased surface area of these structures allows for a variety of new applications beyond conventional emulsion latexes, such as adsorbents and receptor binders for biomedical compounds [1].

In all of these reaction systems there is a definite need to understand the details of the underlying mechanisms in order to control the final product. A number of models for free-radical polymerization kinetics have been proposed, and all depend on the location of monomer relative to the growing polymer chain. This partitioning of monomer determines the overall rate of reaction as well as the dominant free-radical termination events. The widely different initial microstructure of emulsion, microemulsion, and micellar systems leads to important differences in the localization of monomer and polymer. Typical experiments attempt to correlate the overall rate of reaction with the initial and final properties of the microemulsion and latex respectively, with little information about the specifics of the compartmentalized monomer and polymer. In order to elucidate the mechanistic details, polymerization reactions can be performed on-line, using Small-Angle Neutron Scattering (SANS) to provide microstructural information as a function of conversion (or time). SANS is well suited to investigate polymerization reactions, non-invasively probing appropriate length scales in as short as one-minute intervals (Fig. 1).

A microemulsion polymerization of hexyl methacrylate was performed on-line using SANS while simultaneously measuring the conversion [2]. Representative SANS spectra at increasing conversion are shown in Fig. 2. As the reaction proceeds, the diminishing peak in the spectra shows the smooth decrease in the size of the monomer-swollen microemulsion droplets. Simultaneously, the increase in the low- q scattering indicates a steady growth of latex particles.

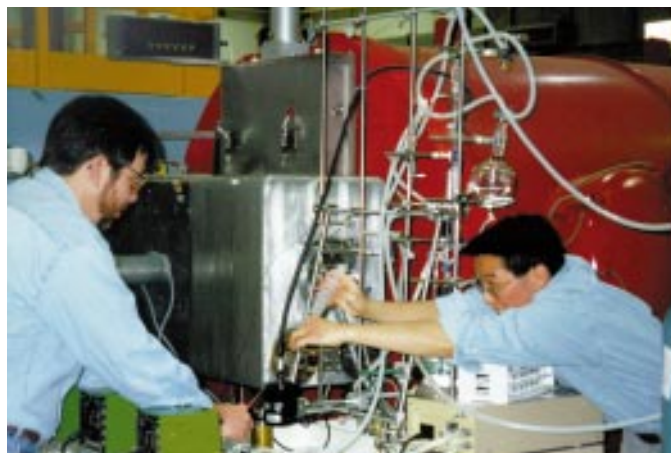


FIGURE 1. Prof. Kaler (L) and graduate student Carlos Co (R) withdraw a polymerization sample for SANS measurement.

Quantitative modeling shows that the average diameter of the latex particles remains nearly constant, simply increasing in number with time. These results support a model of polymerization in which the propagation reaction occurs in a monomer-rich shell surrounding a growing polymer particle that is not swollen with monomer. It also provides insight into the behavior of monomers with different partition coefficients.

Micelle polymerization should behave even less like an emulsion polymerization than a microemulsion. There is now no monomer to partition, since the surfactant is the monomer and is constrained to a specific location in the aggregate. If there is no transfer of monomer between aggregates during the polymerization, the process can be thought of as a “zippering” of the individual micelles.

Unlike most microemulsions, micellar aggregates are not limited to globular structures. In particular, cylindrical surfactant structures can be polymerized. The surfactant cetyltrimethylammonium 4-vinylbenzoate forms viscoelastic solutions in water containing cylindrical micelles of 4 nm diameter and thousands of nanometers long. The SANS curves in Fig. 3 show the evolution of structures from the initial charged micelles to the final polymerized cylinders. At intermediate (20% - 70%) conversion the reacting system passes through a highly turbid and ordered phase, with a sharp peak indicating a well-defined spacing of 5 nm. The ordered phase abruptly disappears, resulting in a stable

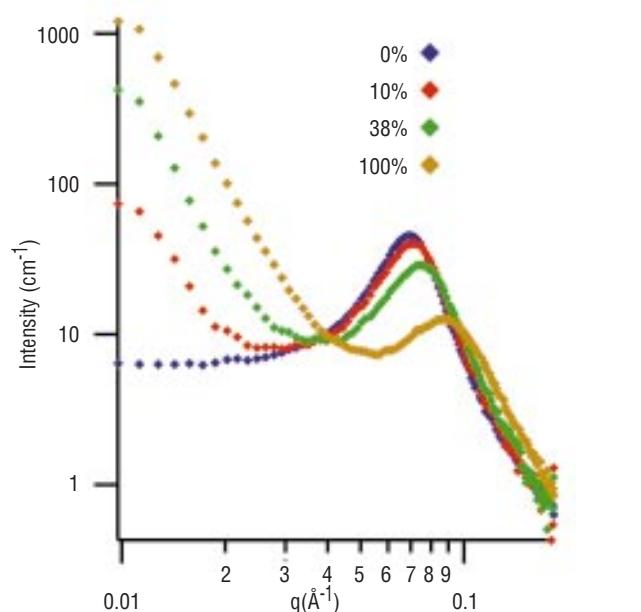


FIGURE 2. SANS spectra of the polymerizing hexyl methacrylate microemulsion as a function of monomer conversion.

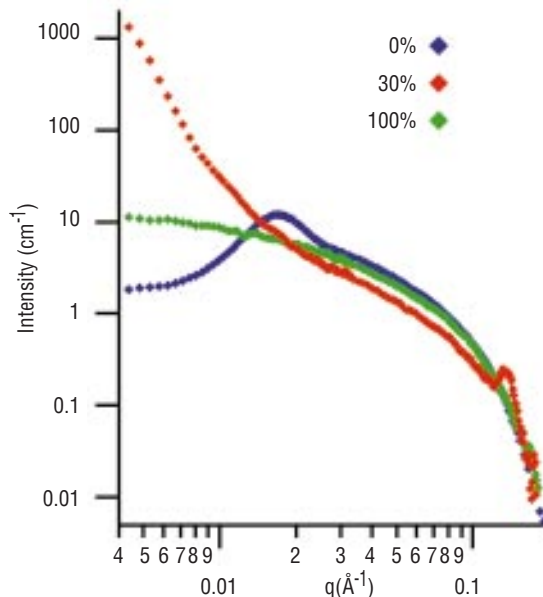


FIGURE 3. SANS spectra of the polymerizing cetyltrimethylammonium 4-vinylbenzoate micelles as a function of time (increasing conversion).

dispersion of discrete, polymerized cylinders 4 nm x 80 nm [3]. This novel ordering behavior is not fully understood, but is in sharp contrast to the smooth structural changes seen in microemulsion polymerization. On-line polymerization SANS measurements provide a visualization of the evolving microstructure that cannot be provided by other methods, permitting validation of polymerization mechanisms.

REFERENCES

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- [3] S. R. Kline, private communication.